

VISUAL LINES
FOR
SPECTRUM ANALYSIS

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A.R.C.S., B.Sc., D.I.C.

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VISUAL LINES *for* SPECTRUM ANALYSIS

BY

D. M. SMITH,

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PREFACE

The value of the spectrometer in analysis seems to be somewhat underestimated, in spite of the ease and rapidity with which metals can be identified when present either as constituents of, or minute impurities in, a great variety of substances. This may be due to the fact that suitable tables of wavelengths of the most sensitive lines (i.e. the lines which appear in the spectrum when only small quantities of a metal are present) are not available in convenient form. This booklet is designed to supply such tables and to give such information as will enable the use of the Wavelength Spectrometer to be adopted in the routine of chemical laboratory practice.

The technique, advocated and practised by Sir Herbert Jackson, F.R.S., is described in detail, and the sensitive lines of 52 elements have been investigated. Various applications of the method of analysis are described, and many variants of these would suggest themselves to anyone using this method.

Criticism of the results put forward, and further suggestions will be welcomed. It is hoped that the usefulness of this booklet will be increased by the correction, in the next edition, of any errors of omission or commission which may be pointed out.

The author gratefully acknowledges the facilities and experience placed at his disposal by Sir Herbert Jackson, F.R.S. (Director of The British Scientific Instrument Research Association) and F. Twyman, Esq., F.R.S. (Managing Director, Adam Hilger Ltd.)

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WAVE-LENGTHS.

“ The position of a line in the spectrum is most generally indicated by the wave-length (λ) of the vibrations which produce it. The unit of wave-length is the Ångström Unit, or ‘angstrom,’ as it is now beginning to be called. It was intended to equal 10^{-10} metre, and is accordingly often called the ‘tenth-metre.’ It is also equivalent to 10^{-8} cm., or 0.0001μ , where μ is the micron, or thousandth of a millimetre. Wave-lengths in the visible spectrum range from about 3900Å to 7600Å (Å being the modern abbreviation for the angstrom). For the long waves in the infra-red, however, μ is often taken as the unit, so that λ 12,500Å, for example, would be indicated by 1.25μ .

“ The wave-length scale was introduced by Ångström in 1869, and until about the year 1900, wave-lengths were referred to his determinations as standards; they were meant to represent the wave-lengths in air at 16° C. and 760 mm. pressure. Later work, however, proved that Ångström’s values were about 1Å too low, and, about 1896, the scale was superseded by that of Rowland, which referred to wave-lengths in air at 20° C. and 760 mm. Still more recently it has been found that Rowland’s scale was based upon erroneous values for the *D* lines of sodium, besides being affected by other small errors, and Rowland’s scale is now being gradually replaced by the ‘International’ scale. The latter is founded upon interferometer determinations of the wave-length of the red line of cadmium, which is much superior to the sodium lines in point of sharpness. The wave-length adopted for this line by the International Solar Union is 6438.4696, being the value determined by Benoit, Fabry, and Perot, and in close accordance with a previous measurement by Michelson. The precision of this value for the standard line is such that the unit of wave-length which it defines can differ but little from 10^{-10} m., but to avoid all misunderstanding the unit of wavelength defined by the cadmium line has been called the International Angstrom; and is indicated in tables by the letters ‘I.A.’; we thus have

$$\text{I.A.} = \frac{\text{Wave-length of red Cd line in dry air at } 15^{\circ} \text{ C.,} \\ 760 \text{ mm. with } g=980.67}{6438.4696} \dots$$

Extract from *Report on Series in Line Spectra* (1922),
Prof. A. Fowler, F.R.S.

1. INTRODUCTORY.

SEVERAL routine methods of spectroscopic analysis by photographing the arc and spark spectra of materials have been developed (see references on pages 32-34). There are, however, very many instances where a visual examination is to be preferred, either on account of the much shorter time involved in the experiment, or because of the evanescence of the traces sought, or because the materials to be examined cannot readily be made the electrodes for an arc or spark.

When electric current was not readily available and batteries had to be used, spectroscopic analysis in the chemical laboratory was generally carried out by dissolving the substance under examination in a suitable solvent and examining the spark obtained from this solution. The use of the arc, on account of the comparatively large amount of current necessary, was seldom resorted to in the days of batteries, and by the time that electric mains became general the trouble involved in using the spark, the poor illumination frequently obtained from it, and indeed the difficulty in many solutions of finding the traces sought, had all combined to put the spectroscope in the position of being the last resort in chemical laboratory practice instead of, as it should have been, one of the first instruments to be employed.

It seems to have become customary to limit the employment of spectroscopic methods to the use of a small Direct Vision spectroscope in the examination of flames and discharges through gases. The spectroscopic method of examining electrical discharges through gases is limited in its application, but the following case of a

residual gas in a valve demonstrates the inadvisability of using a spectroscope with small dispersion.

Using such a spectroscope and examining the white glow in the tube, certain bands were seen which gave the impression that carbon dioxide was present. Further investigation, using a Wavelength Spectrometer, showed that these bands were to be attributed to hydrogen, and no bands attributable to carbon dioxide could be seen. As the Wavelength Spectrometer was fitted with a comparison prism the nature of the gas in the valve was further confirmed by comparing its spectrum with that given by an excited hydrogen tube.

There are but few substances containing metals in some form or other which cannot be spectroscopically examined by means of a carbon arc. The technique is simple and readily carried out.

(We are indebted, for the following description, to Sir Herbert Jackson, F.R.S., Director of the British Scientific Instrument Research Association, who has been in the habit of using the technique constantly for many years.)

2. THE USE OF THE CARBON ARC.

The great value of the spectrometer in analysis is for the detection of small quantities of metallie constituents or impurities, and, with a suitable routine, it may be said almost without qualification that this may be done in any combination of substances. A trial of all the known methods of producing a light source has shown the most useful to be the arc between purified carbon electrodes. The visible spectrum is examined with a Wavelength Spectrometer for lines due to impurities emitted by the substance introduced into the arc.

The most suitable carbons to use are cored carbons about 15 cm. long and 1 cm. external diameter, the

diameter of the core being about 2 mm. On the whole it is an advantage to use a cored carbon for both electrodes. They should be purified by successive soakings in hydrochloric acid of decreasing strengths, after which they are soaked in distilled water. When dried they are ready for use. Ordinary carbons can be purified sufficiently for most purposes in three weeks, providing they do not contain much iron, by soaking for a week in concentrated acid, followed by a week in 1 part acid and 1 part water, and finally by a week in distilled water.

The setting of the Wavelength Spectrometer is made by a polished pointer, illuminated from above by a mirror. The pointer is adjustable laterally by two screws so that changes of zero can be corrected should they occur with lapse of time.

The slide with light filters gives the pointer any desired colour, and this is of great use when observing the violet region of the spectrum as the brightness of the white pointer prevents the eye from observing faint lines. Also, the eyepiece cannot be sufficiently corrected for achromatism throughout the range of the spectrum, so that without such light filters small errors due to parallax are liable to arise.

An instance of the use of the shutters in the eyepiece occurred in testing a precipitate, mainly consisting of mercury, for traces of silver. It was observed that one of the sensitive silver lines (λ 5465.4A) was very near to the strong mercury line λ 5460.7A. By moving the shutters from each side so that the strong mercury line was hidden, the sensitive silver line was more easily detected.

Another example is that of lead containing traces of silver, in which case one of the sensitive silver lines is near the lead line λ 5201.5A.

The accuracy of the spectrometer for wavelength readings having been tested, the pointer in the eyepiece is set on one of the prominent lines of the element

suspected to be present. The image of an arc taking about 5 amps. and of about $\frac{3}{8}$ " length is focussed by a lens on the slit of the spectrometer and the position of the image is arranged so that the images of the white-hot carbons escape the slit. A blank test is made by running the arc for a few minutes to make sure that the prominent line chosen is not visible as a constituent of the purified carbons.

Before making the test in blank, the core of the positive carbon is removed with a small finger drill to a depth of about $\frac{1}{4}$ ". The current having been turned off and the positive carbon having cooled sufficiently, the material under examination is introduced into the cavity of the positive carbon. The arc is again struck and the spectrum examined for the particular line chosen. It will be observed that most of the bands and flutings in the carbon arc spectrum disappear when the substance is introduced into the core of the arc, so that the identification of the sensitive lines is simplified. If the particular line chosen appears, the whole procedure may be repeated and other prominent lines given by the element confirmed in a similar way. The advantage of placing the substance at the bottom of the cavity in the positive electrode is that the vapour of that substance, in whatever form it is given off, must necessarily participate in the emission of radiations from the arc.

In choosing lines for the identification of any particular element, care should be taken that they are not likely to be confused with those due to some other element which may be present in the material under examination. For instance, in testing for zinc in a vegetable substance, line λ 5182.0A should not be chosen, as the almost certain presence of magnesium in the material would give the triplet lines, one of which, λ 5183.7A, would render the identification of the zinc line difficult.

Small pieces of many substances can be introduced without preparation into the cavity of the positive

carbon. Substances which contain a large amount of water should be dried by heating to 100°C . and then powdered in a clean mortar. (An agate pestle and mortar are very convenient.) In some instances it is advisable to incinerate organic substances and to deal with the ash.

Where very minute amounts of impurity are suspected and where chemical processes of separation are inapplicable, it may be advisable or necessary to concentrate the impurity; for example, in testing for minute traces of copper in zinc oxide it is a simple matter to increase the percentage of copper in a portion to be presented to the spectrometer by precipitating the copper along with some zinc. It is, as a rule, unnecessary to attempt to remove the whole of the main constituent, and the tedious process of complete chemical separation is avoided.

When searching the spectrum for faint lines it is often very advisable to open the slit fairly wide so as to allow more light to pass through. Once the presence or absence of that particular line has been established the slit can be closed to the normal width again. This method of using a wide slit is sometimes of great value when observing the blue region of the spectrum, since for the average observer the visibility is not so good in this region.

It is, perhaps, worth mentioning that it is often useful when a particular element is suspected, to introduce a small quantity of that element into the positive of a spare pair of carbons, kept for such a purpose, and to place the pointer very accurately on the particular line chosen for the identification of the element. It will be understood that if the quantity of the suspected element is very small in the material to be analysed, and a line can be seen for a very short time, it may be confused with another line, for example a line in the iron spectrum; the complete removal of this metal from carbon electrodes

is not practicable. This procedure is worth carrying out whenever an element is to be detected, the lines of which are very evanescent. Mereury, for example, in this way has been identified with certainty in a flash of the lines which did not last for more than $\frac{1}{5}$ second. It would be practically impossible in such a short time to identify such an element by a photographic process.

The methods described have been used for many years by one experimenter for the examination of glass, porcelain and many minerals, in addition to the various substances which are met with in the course of chemical analysis.

When the substance under test is in a suitable form (a powder for example) the actual time of making an observation is very short. Using the method of direct comparison (with a pair of spare carbons) the presence or absence of a metal can be determined in a minute or so, in the case of simple spectra.

3. SPECTROSCOPIC OUTFIT

The following outfit has been used in obtaining the data contained in the tables which follow :

D 78. Wavelength Spectrometer (1926 Model),
including F 40-41 Shutter Eyepiece with
slide containing light filters.

F 16. Spherical Glass Condenser.

F 449. Gramont Arc and Spark Electrode Holder.

F 284. Lamp Resistance Board.

F 468. Pure Cored Carbon Electrodes.

(The numbers refer to the catalogue of Adam Hilger Ltd.)

This outfit will suit any ordinary electrical supply (from about 110 volts to 250 volts) A.C. or D.C.

4. WAVELENGTH TABLES FOR USE IN ANALYSIS.

As a preliminary investigation to determine suitable sensitive lines for visual observation and the order of their disappearance, the following procedure was adopted. A small quantity of a metal (or one of its salts) was placed in the crater of the positive electrode, the quantity being sufficient for the spectrum to be well developed. Then the arc was allowed to burn, and as the substance volatilised and the quantity diminished, the order in which the lines disappeared was noted. A similar notation to that used by M. A. de Gramont in his "Tableau des raies de grande sensibilité des éléments" (*Comptes Rendus*, t. 171, p. 1106) has been employed in this case. " τ_1 " denotes the most sensitive line, *i.e.* the last to disappear as the quantity of metal present is decreased, " τ_2 " the next most sensitive line, and so on.

" ν " denotes that the line is one of the most sensitive lines, but the order of disappearance has not been ascertained.

Some quantitative data have been obtained in the following manner. Solutions of soluble metallic salts were made and 10 c.c. of such a solution were added to from 0.5 to 1 gm. of purified precipitated silica, and the whole evaporated to dryness. The silica thus acted as a "blank" containing a certain percentage of the metal, and samples obtained in this way were placed in the carbon arc and the lines appearing in the spectrum which were due to the metal were noted. Various percentages were obtained by successive dilutions of the solutions with distilled water, and the smallest percentage of the metal in the dry mixture, which caused the emission of any particular line, is indicated in brackets in the tables which follow.

Spectroscopic analysis of the silica used as "blanks" showed the presence of traces of sodium, lithium,

titanium and iron, but the metals for which quantitative data is given were absent.

SENSITIVE LINES OF THE ELEMENTS
(*in the Visible Spectrum*).

In the tables which follow, the meaning attached to the word "lasting" is that the line remains visible for a considerable time. This word is used in preference to "persistent" as the latter has been used with a different connotation by Hartley, Pollok and others who photographed the spark spectra of solutions and noted the order of disappearance of the photographically sensitive lines.

All the wavelengths are in International Angstrom units.

Element.	Symbol.	Page.	Element.	Symbol.	Page.
Aluminium	Al	15	Molybdenum	Mo	20
Barium	Ba	15	Neodymium	Nd	21
Beryllium	Be	15	Nickel	Ni	21
Bismuth	Bi	15	Osmium	Os	21
Boron	B	16	Palladium	Pd	21
Cadmium	Cd	16	Platinum	Pt	21
Cæsium	Cs	16	Potassium	K	21
Calcium	Ca	16	Rhodium	Rh	22
Cerium	Ce	16	Rubidium	Rb	22
Chromium	Cr	16	Ruthenium	Ru	22
Cobalt	Co	17	Samarium	Sm	22
Copper	Cu	17	Scandium	Sc	22
Erbium	Er	17	Silver	Ag	23
Gallium	Ga	17	Sodium	Na	23
Germanium	Ge	17	Strontium	Sr	23
Gold	Au	17	Tantalum	Ta	23
Hafnium	Hf	17	Thallium	Tl	23
Indium	In	18	Thorium	Th	24
Iridium	Ir	18	Tin	Sn	24
Iron	Fe	18	Titanium	Ti	24
Lanthanum	La	18	Tungsten	W	24
Lead	Pb	19	Uranium	U	24
Lithium	Li	19	Vanadium	Va	24
Magnesium	Mg	19	Yttrium	Yt	25
Manganese	Mn	20	Zinc	Zn	25
Mercury	Hg	20	Zirconium	Zr	25

NOTES.

ALUMINIUM.

The lines $\lambda\lambda$ 3961.5 and 3944.0 due to aluminium are seen in the arc spectrum when a small quantity of metallic aluminium is placed in the positive electrode. Visibility in this part of the spectrum is not so good, however, and for traces of this element the lines are difficult to observe.

The following bands, due to aluminium oxide are more easily identified, and serve as a means of detecting this element. (The wavelengths of the "heads" of the bands are given.) These bands fade towards the red end of the spectrum.

5079.5 v_2	} These bands are visible with 0.03%	Al.
4842.4 v_1		
4648.1 v_3		
4470.6		

BARIUM.

6496.9	4934.1 v_1	This line is near the caesium line λ 4555.3.
6141.8	4554.0 v_2 .	
5535.5 v		

BERYLLIUM.

This metal gives a band spectrum very similar in appearance to that of aluminium, the wavelengths of the "heads" of the bands of beryllium being :

5056.4	4709.0 v_1
--------	--------------

These bands fade towards the red end of the spectrum. There is also a sensitive line λ 4572.7.

It is difficult to detect beryllium and aluminium when they occur together on account of the overlapping of the two sets of bands.

BISMUTH.

5552.2 v_2	This line is very near to the zinc line λ 4722.2.
4722.5 v_1	

NOTES.

BORON.

The band at λ 5478, due to boron oxide, is the most characteristic indication of the presence of the element. It is particularly noticeable when the flame of the are is focussed on to the spectrometer slit. The band is very diffuse.

CADMIUM.

6438.5	4799.9 v
5085.9 v_1	4678.2

CAESIUM.

4593.2 v_2	4555.3 v_1
--------------	--------------

CALCIUM.

6493.8	} These two groups are visible with 0.06% Ca.
6462.6	
6439.1	
6162.2 v	
6122.2	
6102.7	
4302.5	
4226.7 v_1	

The lines $\lambda\lambda$ 6162.2 and 4226.7 are visible with 0.01% Ca.

CERIUM.

4628.2		4539.7
4593.9	This line is near the caesium line λ 4593.2.	4523.1
		4382.2
4572.3		4320.7
4562.4		4306.7

CHROMIUM.

5409.8		4289.7
5208.4	} Distinctive triplet.	4274.8
5206.0		4254.3
5204.5		

NOTES.

COBALT.

4867·9	4792·9
4840·3	4780·0
4813·5	

The above lines form a distinctive group.

4121·3	4110·5
4118·5	

COPPER.

5782·2	5153·3
5700·2	5106·6 ν
5218·2	

These sensitive lines last for a considerable time.

ERBIUM.

The sensitive lines of this element are not very lasting.

4675·8	4419·8
4375·0	

The sample of Erbium investigated contained some Yttrium, which was detected by means of the most lasting Yttrium lines.

GALLIUM.

4172·1	4033·0
--------	--------

GERMANIUM.

4685·9

GOLD.

6278·2	5064·6
5837·4 ν_2	4792·6 ν_1

HAFNIUM.

No hafnium lines were seen in the spectrum of a very small sample of hafnium oxide, but a band at about λ 5075 occasionally appeared.

NOTES.

INDIUM.

4511.3 v_1	4101.8 v_2
--------------	--------------

IRIDIUM.

5894.1	5364.3
5625.6	4938.1
5449.5 v_1	

IRON.

The following lines often appear in the spectrum of the arc between purified carbon electrodes and are very lasting lines :

5371.5 v	5232.9	4404.8
5328.0 v	5227.2	4383.5
5269.5 v_1		

For quantities of iron greater than 1% the spectrum tends to become confusing on account of the large number of iron lines which are present.

The following distinctive group is present with 0.1% Fe :

4957.6 (6) } (0.004%)	4891.5 (6) } (0.004%)
4957.3 (4) }	4890.8 (4) }
4939.7 (3)	4878.2 (3)
4938.8 (1)	4872.1 (4) }
4920.5 (6) } (0.004%)	4871.3 (5) }
4919.0 (5) }	4859.8 (4)
4903.3 (2)	

The comparative intensities of the iron lines forming this group are given (as they appear in the spectrum of pure iron), the intensity scale being from (0) to (10), (10) denoting the strongest line.

LANTHANUM.

4922.0	4430.1
4900.1	4333.9

NOTES.

The following bands (the wavelengths of the "heads" being given) appear sensitive :

4418

4372

These bands fade towards the red part of the spectrum.

LEAD.

6002·0

5005·5

5608·9

4168·0

5201·5

4057·8 v_1

LITHIUM.

6707·9 v_1 6103·6 v_2

4971·9 This line is close to the position of the sodium doublet $\lambda\lambda$ 4982·9 and 4978·6.

4603·2

The line λ 6707·9 is almost as sensitive as the sodium D lines, and this should be remembered when testing materials for this metal. If some lithium salt is volatilised into the air by means of a carbon arc, all subsequent materials investigated by means of an arc using fresh carbons will show a trace of lithium due to the extremely small amount in the atmosphere surrounding the electrodes.

MAGNESIUM.

5528·4 v_2 (0·01 %)

5183·7

5172·7 v_1 (<0·0007 %)

5167·4

4703·0

4571·2 This line is near the beryllium line
 λ 4572·7.

The last two lines are not visible if the amount of Mg. does not exceed 0·2 %.

NOTES.

MANGANESE.

6021·8	} v_2 (0·05%)	
6016·6		
6013·5		
4823·5	v_1 (0·007%)	
4783·4	} v_2 (0·05%)	
4766·4		
4762·4		
4754·0		
4739·0	} Present with 0·5% Mn.	
4727·5		
4709·7		
4034·5	} v_2 (0·05%)	
4033·1		
4030·8		

The lines from λ 4823·5 to λ 4709·7 form a characteristic group.

MERCURY.

5790·7

5769·6

This distinctive doublet is considered superior to the line λ 5460·7 as a means of detecting small quantities of mercury, although the latter lasts after the doublet.

5460·7 v_1

4358·3

4046·6

MOLYBDENUM.

6030·7 v

5888·3 This line is very near to the sodium lines $\lambda\lambda$ 5890·0 and 5895·9.

5858·3

4435·0

5570·5

4411·7

5533·0

4381·7

5506·5

} v_1

NOTES.

NEODYMIUM.

4463·0	4351·5
4451·6	4325·9
4446·4	4303·8 <i>v</i>
4358·4	4156·2

NICKEL.

5476·9 τ_1	5080·5
5081·1	4714·4

There is also a nickel line λ 5892·9 which appears between the two sodium D lines.

OSMIUM.

5857·8	4794·0 <i>v</i>
5523·6	

PALLADIUM.

5547·0	5163·8 <i>v</i>
5542·8	4875·4
5395·3	4817·5
5295·6 <i>v</i>	4788·2

PLATINUM.

5840·1	5369·0
5478·5	5301·0 <i>v</i>
5475·8	5227·6 <i>v</i>
5390·8	

POTASSIUM.

7699·0	5812·7
7664·9	5802·2
6939·0	5782·8
6911·3	4047·2 <i>v</i>
5832·3	4044·1 <i>v</i>

NOTES.

RHODIUM.

6752·4	5193·1
5599·4 v	4851·6
5379·1	4675·0
5354·4 v	4528·7

RUBIDIUM.

7947·6 v	5724·0
7800·3 v	4215·6
6298·5	4201·8
6159·8	

RUTHENIUM.

5636·2
5171·0 v_2
5057·3
4869·2
4709·5
4584·5

4554·5 v_1 This line is very near the sensitive
barium line λ 4554·0.

SAMARIUM.

4467·3	4421·1
4434·3 v	4390·9
4424·4 v	

SCANDIUM.

6305·7	
5686·9	
5671·8	
5526·8	
5087·0	} Distinctive group.
5085·5	
5083·7	
5081·6	
5031·0	

There is also a scandium oxide band at λ 6036·5.

NOTES.

SILVER.

5471.5	v_2	(0.07 %).
5465.4	}	v_1 (0.01 %).
5209.0		
4668.5	}	Not visible with 0.8 % Ag.
4212.0		

SODIUM.

6160.7	}	v_3
6154.2		
5895.9	}	v_1
5890.0		

This doublet is extremely lasting, and is almost invariably present in the spectrum of the purified carbon electrodes.

5688.2	}	v_2
5682.7		
4982.9	}	v_4
4978.6		

STRONTIUM.

4962.2	
4607.3	v_1
4215.5	This line is near the rubidium line λ 4215.6.
4077.7	

TANTALUM.

6516.1	6045.4 v
6485.4 v	5997.2 v
6430.8	5811.1
6396.8	

THALLIUM.

6549.8
6713.7

These lines are only present when comparatively large amounts of thallium are present, and the line λ 5350.5 is very intense.

5350.5 v_1

NOTES.

THORIUM.

5049·9	4920·0
5017·4	4863·4

TIN.

5631·7	4524·0
--------	--------

TITANIUM.

Distinctive group :

5016·2	4999·5
5014·3	4991·1
5007·2	4981·7

TUNGSTEN.

5514·7	5053·3
5492·3	4302·4
5224·7	4294·7

URANIUM.

The spectrum of this element can be recognised when present in fair quantity by its numerous lines and continuous background.

6862·9	5527·8
6449·2	5492·9
5915·6	5027·6

VANADIUM.

Distinctive groups :

4881·6	4408·5
4875·5	4408·2
4864·8	4407·7
4851·5	4406·7
	4400·6
	4395·2
	4384·7
	4379·2

NOTES.

YTTRIUM.

5663·0		4900·1	
5205·7	} v_2	4883·7	} v_1
5200·4		4674·8	
5087·4		4643·7	
		4375·0	

ZINC.

6362·3	(0·09%)	4722·2	(0·01%)
4810·5	v_1 (0·01%)	4680·2	(0·02%)

ZIRCONIUM.

4815·6	4710·1
4772·3	4687·8
4739·5	

5. SOME EXAMPLES OF THE DETECTION OF TRACES OF METALLIC IMPURITIES IN INORGANIC PRECIPITATES AND RESIDUES.

For the purpose of obtaining the following quantitative data, samples for spectroscopic investigation were carefully prepared by the British Scientific Instrument Research Association in the following way. To a solution of a metallic salt was added a small quantity of a salt of the impurity to be investigated, and the whole was evaporated to dryness. A residue was obtained which had metals present in the proportion of $\frac{1}{10,000}$ or $\frac{1}{100,000}$. This was used as the sample under investigation.

In the following tables the wavelengths of the lines due to these amounts of impurity are given. These tables can be used for the examination of precipitates for impurities. To prepare a precipitate for spectro-

NOTES.

scopic examination, all that is necessary is to dry it. Together with the sensitive lines visible with the amounts stated, notes are included on any points of interest, such as neighbouring lines due to other elements.

IMPURITY.

MERCURY SALT.

- 0·001% Pb. λ 4057·8 just visible.
 0·001% Ag. No lines observed.
 0·01% Ag. $\lambda\lambda$ 5465·4 and 5209·0 faintly visible.
 The line λ 5465·4 is near the strong mercury line λ 5460·7.

SILVER SALT.

- 0·001% Pb. λ 4057·8 just visible.

LEAD SALT.

- 0·001% Ag. No lines observed.
 0·01% Ag. $\lambda\lambda$ 5465·4 and 5209·0 faintly visible. The silver line λ 5209·0 appears near the lead line λ 5201·5.
 0·001% Cu. The following lines are present, but mostly faint :

5106·6	5218·2
5153·3	5782·2

 0·01% Cu. The above lines are visible, with the addition of λ 5700·2.

COPPER SALT.

- 0·001% Cd. λ 5085·9 present for a short time.
 0·01% Cd. λ 4678·2, 4799·9, and 5085·9 present but somewhat evanescent. There is a calcium line λ 6439·1 near the cadmium line λ 6438·5, and hence this cadmium line should be carefully identified if utilised.
 0·001% Pb. λ 4057·8 visible. There is a strong copper line at λ 4062·8.

IMPURITY.	ZINC SALT.
0.01 % Cd.	$\lambda\lambda$ 5085.9 and 4799.9 present. There is a strong zinc line at λ 4810.5.
0.001 % Cd.	λ 5085.9 faintly present.

	BARIUM SALT.
1 % Ca.	All the listed sensitive lines are present, but λ 4302.5 Ca. is masked by λ 4304.9 Ba.
1 % Sr.	$\lambda\lambda$ 4607.3 and 4215.5 are present.

	CALCIUM SALT.
1 % Ba.	$\lambda\lambda$ 5535.5, 4934.1 and 4554.0 are present.
1 % Sr.	$\lambda\lambda$ 4607.3 and 4215.5 are present.
0.01 % Mg.	$\lambda\lambda$ 5183.7, 5172.7 and 5167.4 are present.

	MAGNESIUM SALT.
0.01 % Ca.	λ 4226.7 present.

6. THE DETECTION OF IMPURITIES IN GLASS.

An application of the spectroscopic method of analysis is the detection of the metallic constituents of glasses. The chemical methods for obtaining information on the metals or metallic compounds to which a particular glass owes its colour, may be difficult and are generally tedious. The spectrometer will rapidly detect the metals present as impurities or introduced for the purpose of colouring.

An excellent example is given by the differentiation of three red glasses. Glasses containing gold or selenium or a flashed copper glass may have much the same colour, but on examining the spectrum obtained by fusing a small quantity of glass in the carbon arc, the following lines were seen.

Red Gold Glass.

The line λ 4792·6 was visible, but very faint.

Flashed Red Copper Glass.

All the listed sensitive copper lines were visible. (The copper line λ 5782·2 is very near the potassium line λ 5782·8.)

A small quantity of tin was detected in a sample of this glass, the lines λ 5631·7 and 4524·0 appearing faintly.

Selenium Red Glass.

No lines indicating the presence of selenium were seen, but cadmium is usually present with the selenium. With 1·5% cadmium present the following lines were seen :

λ 5085·9 4799·9 4678·2.

Thus, if neither gold nor copper are detected in a sample of red glass, that glass will probably be a selenium glass, and this conclusion will be strengthened if a trace of cadmium is detected.

Some care has to be taken in introducing the glass into the arc, as the heat may splinter the glass and cause it to fly out. The best procedure is to place a small piece of the glass in the cold cavity of the positive carbon and close the arc till the negative carbon is in contact with the glass. Then the arc is struck by means of a spare carbon and the glass gradually fuses into a small globule. On opening the arc and observing the spectrum the sensitive impurity lines can be identified. For the analysis of glasses it seems that a very short arc will prove most effective.

In every sample of glass tested, titanium has been detected. Purified precipitated silica also contains a small quantity of this element, and it appears that silica is invariably accompanied by traces of titanium.

If the yellow colour of a sample of glass is due to uranium, the lines $\lambda\lambda$ 5527·8, 5492·9 and 5027·8 will be present (but faint); and if it is due to cadmium, the line λ 5085·9 will flash up in the spectrum.

Copper blue glass is identified by the presence in the spectrum of all the listed sensitive lines.

Nickel can be detected in glass by means of the following lines :

5476·9	5080·5
5081·1	4714·4

A further example is the detection of 1% lead in soda glass, by means of the line λ 4057·8.

Chromium is readily detected in chromium green glass, all the sensitive lines listed appearing in the spectrum.

7. MISCELLANEOUS APPLICATIONS OF THE DETECTION OF METALLIC IMPURITIES.

(a) *Organic Substances.*

The detection of metallic impurities in organic substances, such as vegetable matter, is a useful application of spectroscopic methods. Metallic compounds added as preservatives or colouring matter may be detected, and the purity of foodstuffs controlled. For example, 0·06% zinc and 0·05% copper is readily detected in peas. Before introducing the peas into the arc they are first dried and powdered.

(b) *Inorganic Substances.*

1% of magnesium can be detected in kaolin. The spectrum of the arc when kaolin is introduced into it shows the bands of aluminium oxide very pronounced, and the band 5079·5 tends to mask the sensitive magnesium lines. The silica is accompanied, as it invariably seems to be, by a small quantity of titanium.

The detection of traces of mercury which had penetrated the fused-quartz tube of a mercury arc lamp has been carried out by observing the flash of the lines $\lambda\lambda$ 5790.7 and 5769.6. The fused quartz was heated to a bright red-heat for some time to drive off any adherent mercury from the surface before being placed in the arc.

8. APPLICATION OF THE WAVELENGTH SPECTROMETER TO THE DETECTION OF IMPURITIES IN METALS.

A further application of the visual method is to be found in the determination of metallic impurities in metals and alloys. It should be pointed out, however, that for general metallurgical work the photographic method of analysis is superior. An arc is obtained between two pieces (such as metallic rods) of the substance under investigation and, providing the spectra of such metals and alloys are not complex, they can be examined by means of the Wavelength Spectrometer D 78.

Several instances of a semi-quantitative nature have been investigated in this way.

(a) *Impurities in Zinc.*

Using a series of graded zinc-cadmium alloys, the following table was constructed from an investigation of their arc spectra. A current of approximately 1.5 amperes was used, maintaining an arc of $\frac{3}{16}$ " length.

λ	0.75% Cd.	0.1% Cd.	0.016% Cd.	0.01% Cd.	0.001% Cd.
6438.5	<i>p</i>	<i>f</i>	<i>f</i>	—	—
5085.9	<i>p</i>	<i>p</i>	<i>p</i>	<i>f</i>	<i>bv</i>
4799.9	<i>p</i>	<i>f</i>	<i>f?</i>	—	—

where *p* = present ; *f* = faint ;
bv = barely visible.

The line λ 4057.8 of lead appears in the arc spectrum of zinc containing 0.1% Pb.

0.01% iron can be detected in zinc by means of the lines :

5371.5	5232.9	4404.8
5328.0	5227.2	4383.5
5269.5		

(b) *Impurities in Copper.*

The following cadmium lines were present in the arc spectrum of a sample of copper containing 1.16% Cd :

$\lambda\lambda$ 6438.5 (faint).

5085.9

4799.9

4678.2 (near to the copper line, λ 4674.8).

The bismuth line λ 4722.5 is present in the spectrum of copper containing 0.01% Bi. If zinc is present, this line is indistinguishable from λ 4722.2 of zinc, but in this case another distinctive zinc line λ 4810.5 will also be present.

(c) *Brass containing Aluminium.*

No lines due to aluminium were detected in the arc spectrum of a sample of brass containing 0.64% aluminium, but the aluminium oxide band, the wavelength of whose "head" is λ 4842.4, was readily distinguished.

(d) *Lead containing Tin.*

1% of tin can be detected in lead by means of the lines $\lambda\lambda$ 5631.7 and 4524.7.

(e) *Steels.*

The dispersion of the spectrometer D 78 is insufficient for the determination of impurities in ferrous metals and alloys, such as steels, and a dispersion such as is given by the Large Model Spectrometer D 19 is necessary. Nickel can be detected in steels using this latter instrument.

A special instrument has been designed for the detection of nickel and chromium in steels (D 59-61). The instrument has no adjustments, the observation of nickel and chromium lines respectively being made by two eyepieces, in one of which are seen the most distinctive nickel lines ($\lambda\lambda$ 5081.1 and 5080.5) and in the other the most distinctive chromium lines ($\lambda\lambda$ 4289.7, 4274.8 and 4254.3). The nickel doublet is very similar in appearance and close to the iron doublet $\lambda\lambda$ 5079.7 and 5079.2.

REFERENCES TO SPECTROSCOPIC ANALYSIS BY PHOTOGRAPHY.

RESEARCHES OF HARTLEY, POLLOK AND LEONARD.

These researches on the spectroscopic analysis of solutions were published in *Roy. Soc. Phil. Trans.*, 1884, parts (i.) and (ii.), and in *Roy. Dublin Soc. Proc.*, vol. xi. (N.S.), Nos. 16, 17, 18, 23, 24, 31 (1907-9) and vol. xv. (N.S.), No. 25 (1918). The tables of the "persistent" lines (the lines of an element which remain in the spectrum as the amount of that element decreases) are reproduced in *Wavelength Tables for Spectrum Analysis* (Adam Hilger Ltd.).

RESEARCHES OF M. A. DE GRAMONT.

The results of M. A. de Gramont are to be found almost entirely in a long series of papers in the *Comptes Rendus*, vols. 144 to 175. They are summarised by him in the *Comptes Rendus*, vol. 171, p. 1106; and the table there given is also reproduced in *Wavelength Tables for Spectrum Analysis* (Adam Hilger Ltd.). M. le Comte de Gramont, shortly before his death, kindly corrected the proofs of this reproduced paper, and in so doing, corrected some errors which appear in the *Comptes Rendus*.

“SPECTRUM ANALYSIS IN AN INDUSTRIAL LABORATORY.”
(*Trans. Amer. Inst. Mining and Metallurgical Engrs.*, No. 1134-N. Feb. 1922.)

The application of a Quartz Spectrograph to the detection of impurities in materials in a qualitative manner is described, and illustrated with examples where the method is superior to chemical analysis.

“PRACTICAL SPECTROGRAPHIC ANALYSIS.” (*Bur. Stand.*, vol. 18, Sci. Paper No. 444. July 1922.)

A detailed description is given of the apparatus and technique for making quantitative analyses by means of the spectra of condensed sparks. Illustrated examples of the method are given in the case of impurities in tin, gold and platinum.

“METALLURGICAL SPECTRUM ANALYSIS.” (*Jour. Soc. Chem. Ind.* April 1927.)

A brief review of the history and development of Spectrum Analysis is followed by a description of the technique and possibilities of the quantitative determination of impurities in metals by means of the Quartz Spectrograph. Illustrated examples are given of the quantitative determination of calcium in magnesium and certain impurities in steels.

“SOME USEFUL APPLICATIONS OF A QUARTZ SPECTROGRAPH.” (*Paper presented to the Amer. Soc. for Testing Materials*, June 1927.)

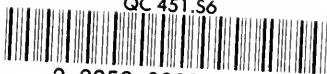
This paper mainly discusses the qualitative applications of the spectrograph, and emphasizes the economy in time and inventory which result therefrom. Some indications of a quantitative nature are also given.

“QUANTITATIVE SPECTRUM ANALYSIS.” (*Paper presented to the Inst. of Metals Divn. of the Amer. Inst. of Mining and Metallurgical Engrs., Sept. 1927.*)

The matter in “Metallurgical Spectrum Analysis” (reference above) has been amplified, and the paper includes the quantitative determination of cadmium, lead and iron in zinc.

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Smith, Donald Murgatroyd.
Visual lines for spectrum analysis,
by D. M. Smith. London, A. Hilger ltd.
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34 p. 22 cm.



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